Re-entrant Behavior and Gigantic Response in Disordered Spin-Peierls System

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Effects of disorder and external field on the competing spin-Peierls and antiferromagnetic states are studied theoretically in terms of the numerical transfer matrix method applied to a quasi one-dimensional spin 1/2 Heisenberg model coupled to the lattice degree of freedom. We show that, at temperatures above the impurity-induced antiferromagnetic phase, inhomogeneous spin-Peierls lattice distortions remain to exist showing a re-entrant behavior. This feature can be drastically altered by very weak perturbations, e.g., the staggered magnetic field or the change in interchain exchange coupling $J_\perp$, leading to a huge response, which is analogous to the colossal magnetoresistance phenomenon in perovskite manganese oxides.

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In strongly correlated electronic systems, various kinds of long ranged ordered (LRO) phases emerge, frequently those energies being very close to each other, i.e., with multicriticality. In such cases, the system becomes sensitive to perturbations such as applied pressure, magnetic field, electric field, carrier/impurity doping, etc., leading to intriguing new phenomena.

The disordered spin-Peierls (SP) system realized in doped $CuGeO_3$ [1] is a typical example showing such subtle multicriticality of different phases. Its phase diagram on the plane of temperature, T, and impurity concentration, x, is experimentally explored in detail (Fig. 1(a)), which is almost universal regardless of the dopant substituting for either Cu or Ge sites [2]. The nonmagnetic SP state realized in undoped $CuGeO_3$ is fragilely destabilized by impurities of a few percent, as shown in Fig. 1(a). The impurities induce local spin moments where the interchain exchange coupling results in the antiferromagnetic (AF) state, which, at the small-x and low-T region, co-exists with SP lattice distortion in an inhomogeneous way (SP+AF phase in Fig. 1(a)) [3]. On the other hand, when x is rather larger, a uniform AF state with homogeneous staggered spin moments becomes stabilized. The critical region between the phases is slightly sensitive to the dopant, where the system shows either bicritical behavior between the SP and AF states, or tetracritical behavior between all the three phases [2], though these are not thoroughly traced by experiments. Fig. 1(a) shows the former case with a bicritical point. Theoretical aspects of this system are also intensively studied analytically [4–8] as well as numerically [9], mostly to understand the novel co-existent state at the small-x region, while a few mention the large-x region [7,8].

Another typical example of such interplay between multicriticality and disorder in strongly correlated electron systems is the colossal magnetoresistance (CMR) in perovskite manganese oxides $R_{1-x}A_x MnO_3$ (R: triva-
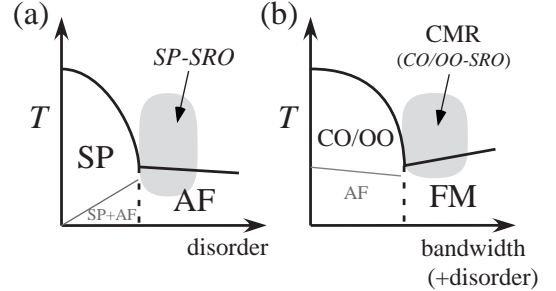

FIG. 1. Schematic experimental phase diagrams for (a) disordered SP system [2] and (b) manganite oxides showing pronounced CMR [14]. The ordinate is temperature, T, while the abscissa represents (a) the degree of disorder realized by increasing the impurity concentration and (b) the substituent concentration controlling not only the degree of disorder but also the bandwidth (for example Ca concentration in $Sm_{0.55}(Ca,Sr)_{0.45}MnO_3$ [14]). The grey areas show (a) the region of re-entrant SRO of SP state, and (b) the region with enhanced CO/OO fluctuation and CMR effect.

lent rare earth element, A: divalent alkaline earth element) [10]. CMR is seen in compounds where an insulator-to-ferromagnetic metal (FM) phase transition is observed upon cooling. Small magnetic field can make the characteristic temperature such as the maximum in resistivity drastically shifted to higher temperature, thus resulting in a "colossal" change of the resistivity. To understand this effect, the importance of not only the multicriticality between the FM phase and the insulating charge/orbital ordered (CO/OO) state [11,12], but also the disorder effect due to quenched chemical dopant has recently been pointed out [13,14]. From experiments carefully controlling the degree of disorder in a chemical way [14], the randomness seems to destabilize the CO/OO state resulting in the FM ground state [15] where the CMR effect becomes prominent, as schematically shown in Fig. 1(b). Theoretical works on models

for manganites with randomness have succeeded to reproduce such features [16,17].

Here we point out an analogy between the CMR manganites and the disordered SP system by making a correspondence of the competing phases as CO/OO $\leftrightarrow$ SP and FM $\leftrightarrow$ AF, respectively. As discussed above, the former states are destabilized by impurities, resulting in the latter states. As a matter of fact, their phase diagrams on the plane of T and degree of disorder, as seen in Fig. 1, are isomorphic to each other. In the disordered SP system, above the transition temperature for the uniform AF state, T_{AF}, short range order (SRO) of SP lattice distortion is observed to develop toward T_{AF} while it is suppressed below it, resulting in a characteristic re-entrant behavior [18]. This is also analogous to the CMR compounds where SRO of lattice modulations due to CO/OO, either static or dynamic, are seen above the FM transition temperature [10,14]. The origin of the CMR effect is now believed to be due to the sensitivity of such re-entrant CO/OO fluctuations [13,14,16,17]. Then, similarly, we expect that some "colossal" effect can also be seen in disordered SP system, which is investigated in this Letter.

To study the disordered SP system, we consider a quasi 1D spin 1/2 AF Heisenberg model coupled to the lattice distortions [19,20]. The model consists of 1D chains, each of which being given by the Hamiltonian,

$$\mathcal{H}_{1D} = \sum_i \left\{ J(1 + u_i)\vec{S}_i \cdot \vec{S}_{i+1} + \frac{K_i}{2}u_i^2 \right\} , \qquad (1)$$

while these are coupled by interchain exchange interaction between neighboring chains,

$$\mathcal{H}_\perp = \sum_{\langle i,j \rangle} J_\perp \vec{S}_i \cdot \vec{S}_j , \qquad (2)$$

where $J, J_\perp > 0$. Each chain is the usual SP model if K_i is uniform, which is unstable toward SP lattice dimerization, $u_i = (-1)^i u_{SP}^0$, in order to gain singlet formation energy in spite of the loss in elastic energy in the second term of Eq. (1) [19].

On the other hand, the interchain exchange coupling, $J_\perp$, in Eq. (2) brings about the competing AF state [20], to which we apply the mean field approximation as in Refs. [8,20]. This is justified for quasi-1D system because the correlation length is already large near the transition temperature [21]. Then we obtain an effective 1D model,

$$\mathcal{H}' = \mathcal{H}_{1D} - zJ_\perp \sum_i \left(\langle S_i^z \rangle S_i^z - \langle S_i^z \rangle^2/2 \right), \qquad (3)$$

where z is the number of neighboring chains and the mean field approximation for $J_\perp$ is even exact in the limit of $z \to \infty$ with $zJ_\perp$ being finite. Note that in this formalism the mean field $\langle S_i^z \rangle$ is independent of chain in the original model, and thus consequently u_i too [8].
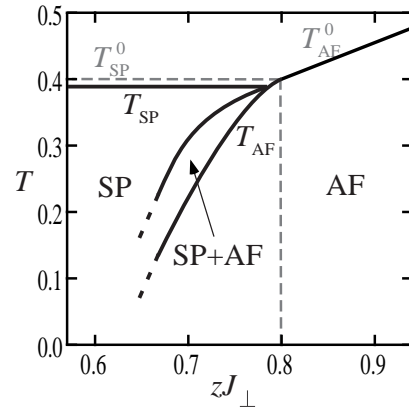

FIG. 2. Theoretical phase diagram for disordered SP system on the plane of T and $zJ_\perp$. The phase boundaries for the pure case are also written as grey broken lines. The AF transition temperature for the pure case, T_{AF}^0, is identical to that in the presence of disorder, T_{AF} for $zJ_\perp > 0.8$.

Impurities are modeled here by replacing the spin-lattice coupling constant, K_i, as $K_{bulk} \to K_{imp}$ randomly [5,8], and the renormalized lattice distortions u_i are treated as classical values. We use the numerical transfer matrix method [22,23] to calculate the finite-T properties of this model, determining u_i and $\langle S_i^z \rangle$ for each site on the chain self-consistently by minimizing the free energy. We use data on open chains with sizes up to $L = 160$ and obtain thermodynamic-limit properties applying extrapolation by $1/L$, and for the random average we take 20-40 samples fixing the impurity concentration. Note that the method looses accuracy at low-T, at about typically $T < 0.1J$, thus our study is complementary to the previous studies on the low-T properties of disordered SP system [4,8]. In the following we set $J = 1$ as the energy unit.

In Fig. 2 we show the phase diagram on the plane of T and $zJ_\perp$ for the case of fixed impurity concentration of 1/8 with $K_{bulk} = 0.8$ and $K_{imp} = 1.5$. In the pure case of $K_{bulk} = 0.8$, drawn by grey broken lines in Fig. 2, a bicritical behavior is seen at $zJ_\perp = 0.8$ between the SP state and the AF state with $\langle S_i^z \rangle = (-1)^i m_{AF}^0$, m_{AF}^0 being the staggered spin moment, naturally understood from the previous studies for the ground state [20]. Here the SP transition temperature, T_{SP}^0, is constant and the AF transition temperature, T_{AF}^0, is linear as a function of $zJ_\perp$, since we treat u_i as classical values and the interchain interaction within mean field approximation. When the impurities are introduced, as can be seen in Fig. 2, the AF state is extended over a certain range of $zJ_\perp$. However, above this uniform AF phase, we observe the SP state and a crossover region in between, where a co-existent state of SP and AF with both order parameters spatially varying is stabilized, represented as SP+AF in Fig. 2. We shall see this in more detail in the following.

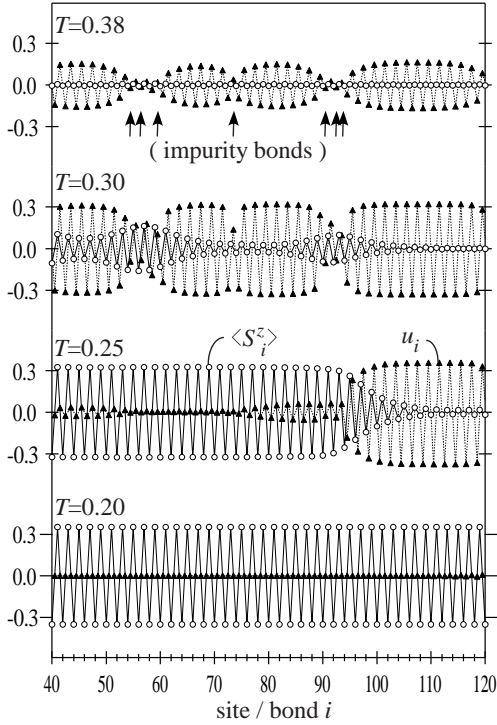As an example, in Fig. 3 the evolution of spatial pat-

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FIG. 3. Spatial pattern of u_i and $\langle S_i^z \rangle$ for a certain sample of $L = 160$ with $zJ_\perp = 0.72$. Only the middle half of the chain ($L/4 < i < 3L/4$) is shown, to omit open boundary effects. The impurity positions with $K_{\text{imp}} = 1.5$ (in the bulk, $K_{\text{bulk}} = 0.8$) are shown by arrows.

FIG. 4. Temperature dependence of u_{SP} and m_{AF} for different values of $zJ_\perp$. Error bars are due to distribution of results from samples with different impurity positions.

tern of u_i and $\langle S_i^z \rangle$ is shown for a certain sample of $L = 160$ for $zJ_\perp = 0.72$. When T is decreased from high temperatures, the SP lattice dimerization is developed from slightly below T_{SP}^0, but the amplitude is modulated such that $|u_i|$ show local minima at the impurity bonds, since $K_{\text{imp}} > K_{\text{bulk}}$ dislikes lattice distortion. When T is lowered further, AF staggered moment starts to emerge, locally nucleated by the impurities out of the SP background, thus co-existing with SP in an inhomogeneous way. We note that although the amplitudes are modulated, the phases of both SP and AF order parameters are unchanged throughout the chain [4,8], i.e., there is no solitonic domain wall structure as discussed in Refs. [5,6,9]. The co-existence only survives at intermediate-T and finally the uniform AF state is stabilized at low-T where u_i becomes zero. This co-existent state is similar to what is observed in slightly doped CuGeO$_3$ at low-T [2,4] (see Fig. 1(a)).

In Fig. 4, the infinite-L extrapolation of the sample averaged SP lattice dimerization and AF spin moment, $u_{\text{SP}} = \langle \frac{1}{L} |\sum_i (-1)^i u_i| \rangle_{\text{av}}$ and $m_{\text{AF}} = \langle \frac{1}{L} |\sum_i (-1)^i \langle S_i^z \rangle| \rangle_{\text{av}}$, respectively, are plotted as a function of T for several values of $zJ_\perp$. In the region of $zJ_\perp$ shown in Fig. 4, first u_{SP} develops as T is lowered where the inhomogeneous SP state emerges, while $m_{\text{AF}} = 0$, as in the sample in Fig. 3. Eventually m_{AF} becomes finite and both orders are stabilized as LRO.
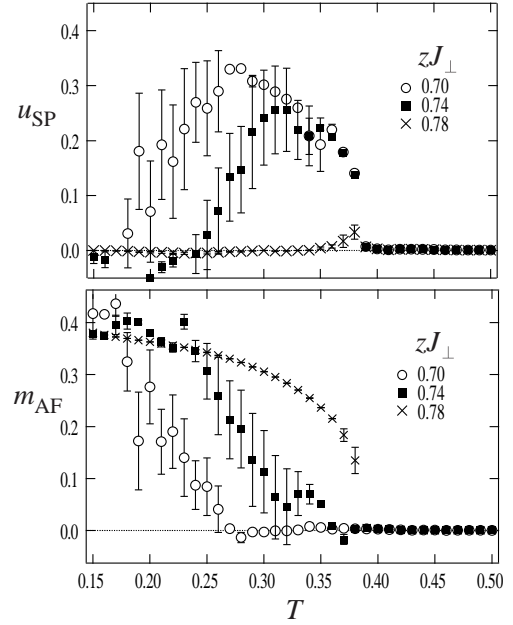
There, as m_{AF} develops, u_{SP} is suppressed, and finally the uniform AF state dominates over the SP state. Although the error bars due to random sample average are rather large, we can clearly see the re-entrant behavior in u_{SP}, the region with co-existence, and the stability of the uniform AF state at low temperatures, to draw the phase diagram in Fig. 2. The slopes of the phase boundaries of the impurity induced uniform AF state and the co-existent state are considerably steep, therefore the states can be shifted drastically with small change of the inter-chain coupling.

Next we apply staggered magnetic field H_s by adding the term, $H_s \sum_i (-1)^i S_i^z$, to the effective 1D model in Eq. (3). We consider this term to control the relative energies of SP and AF states, analogous to the uniform magnetic field in CMR manganites. In Fig. 5, T-dependences of u_{SP} and m_{AF} are plotted for $zJ_\perp = 0.7$, when the staggered magnetic field is varied. With considerably small values of H_s, u_{SP} becomes completely suppressed, and at the same time m_{AF} is drastically increased. The inflection point in the T-dependence of m_{AF}, representing the characteristic temperature for the emergence of AF, is shifted about $\Delta T = 0.2$ to higher-T, which is ten times the energy of the applied staggered magnetic field of $H_s = 0.02$. Thus we have demonstrated that there is actually a "colossal" response in this system.

Now we compare our results to real systems. In doped CuGeO$_3$, in some range of T above the impurity induced uniform AF phase, the static SP lattice distortions show a re-entrant behavior observed by elastic neutron scattering [18] as mentioned previously, similar to what is seen in our calculations (Fig. 4). However in experiments
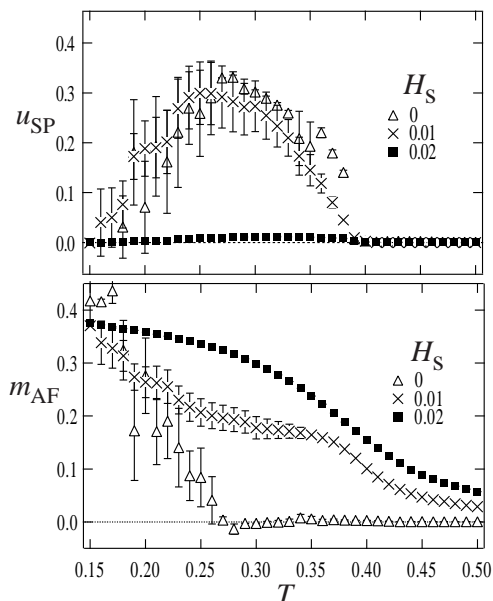
FIG. 5. Temperature dependence of u_{SP} and m_{AF} for $zJ_\perp = 0.7$ under small staggered magnetic field, H_S.

the correlation length remains finite [18], namely, the SP state remains to be SRO, while in our calculations it attains LRO. This discrepancy may be due to the treatment of the impurities in our calculations, such as to ignore effects of the random impurity positions between neighboring chains and/or to assume that the impurity modifies only K_i neglecting the change in the intrachain coupling J. Such effects would make the system more disturbed resulting in frustration for the SP state in the interchain directions as pointed out in Ref. [24], due to solitons of SP order parameters changing the phase at the impurities [5,6,9]. This actually reduces the correlation length of SP order parameter, but the SP lattice distortions would remain static as in the experiments even if such effects were considered. Therefore, we believe that main features of our results are relevant to doped $CuGeO_3$.

We note that another theoretical study in Ref. [7] also showed apparently similar re-entrant behavior in a narrow parameter range. However, because of their weak-coupling continuum treatment with white noise-type disorder, all of their states are with spatially uniform SP and AF order parameters. This is very different from the experiments [2,3,18], as well as from our SP and co-existent states, where we believe that the spatially inhomogeniety is crucial for the emergence of the huge response.

Our observation that very weak perturbation to the system can drive such "colossal" response should be relevant to the actual compounds. Although the staggered magnetic field that we have applied is a fictitious field, perturbations that can change the relative energies of SP and AF states might also produce such drastic changes. For example, the application of pressure, p, is one candidate, through the change in $J_\perp/J$ or K_i resulting in a

large change of the transition temperatures as we have seen in the phase diagram, Fig. 2. In doped $CuGeO_3$, the hydrostatic pressure drives the system toward the stability of SP state, contrary to the usual expectations [19], due to the enhancement of the next-nearest-neighbor exchange along the chains [2,25]. The enhanced dT_c/dp in doped samples compared with the pure sample may be related to the sensitivities of our impurity induced states. Furthermore, an estimate of uniaxial dT_c/dp's in terms of the Ehrenfest relation using the measured specific heat and thermal expansion [26] also gives a large value. The uniform magnetic field might lead to the giant response as well. Up to now, the experiments are mainly done for small-x samples which found no such large change while the system converts into an incommensurate phase [2,27]. Measurements in the multicritical regime are desired.

In conclusion, we have demonstrated that a model of disordered SP system competing with the AF order shows a re-entrant behavior and huge responses to small perturbations such as the staggered magnetic field or the change in the interchain coupling $J_\perp$. This is analogous to the CMR effect in manganites, where the multicritical phenomenon influenced by the disorder leads to the "colossal" response.

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